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Dear Darryl and Frank:

The Council of Great Lakes Industries has reviewed the draft report "Great Lakes
Binational Toxics Strategy Octachlorostyrene Report: A Review of Potential Sources.
We have contacted knowledgeable individuals within most of the industrial sectors
discussed in the report. We and the experts whom we have consulted have found the
report to be very seriously flawed. This letter, and an extensive report to the OCS
Workgroup which, as planned, will follow within the next several days, detail these
findings.

Report Approach

The most serious error regarding this second Battelle OCS report (it follows the initial
draft OCS Action Plan) is its approach to the assessment of the status of Binational Toxics
Strategy (BNTS) challenges regarding OCS. Rather than take an objective view of
whether or not the challenges have been met, the report authors seem to go out of their
way to deliberately seek the most minuscule, insignificant, and theoretical potential
sources. Certainly CGLI expects a rigorous review of source status. But, we expect this
review to be conducted on the basis of confirmation of releases through the use of sound
analytical techniques. When measurements fail to link a "suspected" source with actual
releases, we do not believe it serves any purpose to continue to suggest a "potential"
release based on posed theoretical circumstances. Unfortunately, the report does this in
several places.

A second serious oversight is the failure to investigate and acknowledge the absence of
certain industry sectors within the Great Lakes Basin. The continued use of a particular

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technology at a location far removed from the Basin is not, unless special circumstances prevail, likely to have a significant impact on Basin waters. CGLI's sector review work has shown that several suggested sources or processes do not operate within the Basin. We note that a newly released draft Ontario OCS inventory report, although it may suffer from some of the technical short comings as the Battelle report, does in fact look first to see if the suggested sources are active in Ontario.

As described below, the most serious technical error is the one-size-fits-all approach taken to apply surrogate measurements and calculate potential OCS releases. As explained in the extensive review produced by Mr. Larry LaFleur of NCASI, comments from whom have also been forwarded by the American Forest and Paper Association, the HCB/OCS or dioxin/ocs relationship for a given source is dependent on many variables and must be carefully determined on a case by case basis. In addition, factors like partition coefficients and other important variables must be considered when extrapolations from sediments are made to predict source releases. Mr. Robert Bailey, a member of the HCB Workgroup, has provided the analysis which appears below.

Sector Analysis

CGLI has undertaken a comprehensive review of the OCS sources in the Battelle report on a sector by sector basis. We have contacted industry experts and solicited comments on the basis for which OCS releases have been suggested within the report. This detailed response is in final preparation stages and will be forwarded to the BNTS OCS Workgroup when completed.

Detailed Technical Comments

As mentioned above, Dr. Larry LaFleur of the National Council of the Paper Industry for Air and Stream Improvement has studied the mechanics of chlorinated phenolic compounds extensively. He has reviewed the second Battelle report and has concluded that from a mechanistic and sound scientific process standpoint, the document is seriously flawed. His observations include the following.

Introduction

A fundamental premise of modern synthetic chemistry is that one needs to understand the basic reaction mechanism before one can reliably predict products. Even if one knows the proper mechanism, the appropriate reaction conditions (e.g., temperature, catalyst, sufficient time, proper solvents, suitable concentrations, etc.) must be present in order for the reaction to proceed. Many reactions which occur in one solvent, such as free radical chlorination in aprotic solvents, would be suppressed in a protic solvent such as water. Finally, the necessary starting materials must not only be present, but must be present in proportions conducive to the reaction. In many respects, synthetic chemistry is the science of successfully optimizing the various combinations of these variables to achieve a specific, desired outcome.

Accordingly, any technically creditable extrapolation from known sources of octachlorostyrene (OCS) to potential other sources requires a careful consideration of reaction mechanisms, conditions, and stoichiometry. Thus, sufficient evidence that each of these criteria have been met must be demonstrated before one would have sufficient cause to further examine a hypothesized new source.

Below, we discuss mechanistic considerations, reaction conditions, and stoichiometry of some known sources of OCS. In this discussion, we highlight the types of corroborating data that would be necessary to extrapolate known OCS sources to other sources. We also give several examples of how a more critical consideration of these fundamental principles would show that there are no data to support the hypothesis that these processes are potential sources of OCS. We briefly discuss the Battelle approach to estimating an OCS inventory based on the EPA dioxin inventory and show that the underlying assumptions are fundamentally flawed.

Mechanistic Considerations

Hexachlorobenzene, octachlorostyrene, and PCDD/F

The Battelle report notes an apparent relationship between hexachlorobenzene and octachlorostyrene where PCDD/F have also been reported. These different mechanisms seem to arise where the starting materials and/or conditions are such that hexachlorobenzene can be formed. Apparently, under these same conditions hexachlorobenzene can further react to form octachlorostyrene or it can proceed through a different series of reactions to form PCDD/F. Under these circumstances, there is an apparent relationship between octachlorostyrene and PCDD/F. However, it would be inappropriate to conclude that the reverse would also be true. If PCDD/F are formed by some other mechanism under other conditions, it may or may not coincidentally produce either hexachlorobenzene or octachlorostyrene. As is discussed in Section V, there are several examples of PCDD/F formation where there is no reason to suspect formation of octachlorostyrene.

The de novo synthesis hypothesis

In the review of sources commissioned by EPA in 1985, Schulman and Klingele[1] discussed theoretical mechanisms for octachlorostyrene formation. They proposed the following hypothesis:

"Each reaction in the stepwise formation of PCSs could fall into one of two broad categories:

1. ultratrace concentrations of reactants combine in high yield; or

2. high concentrations of reactants combine in ultratrace yields

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[1] For complete description of references see bibliography contained in Appendix I.

In the former case, the free energy of formation of the product at each step is lower than the free energies of reactants and other competing products. In the latter case, the free energies of formation of reactants and other products are lower than the PCS precursor products, but the statistics of the reaction chemistry assure that some of each of the successive precursor products will be generated in some amounts.

Reaction conditions favoring the former case would probably involve high energy environments where polychlorinated aromatics like PCSs would be stable relative to other molecular configurations. Such conditions would be likely to prevail in high energy electro-, pyro-, photo- and thermochemical reaction environments. Reaction conditions favoring the latter case would involve lower energy reactions in which polychlorinated organic substances are reactants or intended products. Further, if PCSs were removed from the reaction environment fastest than other, more stable products, say via physical processes such as sorption to the walls or bottom of a reactor vessel or to particulate matter in the reaction matrix, significant quantities of PCSs could still be generated, even though not thermochemically favored."

Schulman and Klingele (1985) went on to propose a theoretical mechanism that might lead to the formation of octachlorostyrene through a series of high energy free radical chlorinations and polychloro alkyene radical coupling reactions. This mechanism is termed the *de novo* synthesis mechanism. This mechanism was not proposed based on any experimental investigations on their part, but was instead based on their review of potentially relevant published literature and their interpretations.

Their final conclusions based on their deliberations were:

"Whenever a carbon source is exposed to chlorine and large energy flux, as either electricity or heat, and indicator compounds such as carbon tetrachloride, perchloroethylene, and perchlorobenzene are produced, PCS is a suspected byproduct. Whenever aromatic compounds, particularly chlorinated ones, are exposed to conditions where chloroalkyl radicals may be present, PCS is a suspected byproduct."

We would add to those observations the fact that the chemistries used to support their hypothesis were free radical reactions occurring under extremely high energy conditions, and were often conducted with a very large excess of chlorine (relative to the available carbon). We believe these are important distinctions.

The Battelle report cites this hypothesis, describes it generally, but does nothing to further advance it or support it with new information.

Based on the rationalizations used to advance this hypothesis, the *de novo* mechanism is clearly a high energy free radical chlorination and coupling mechanism. In order to invoke this mechanism for a potential new source of OCS, one should provide supporting data to

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justify the hypothesis. As discussed in the Schulman and Klingele report, one should provide evidence of other intermediates or by-products that support that a similar mechanism is operative. These may include carbon tetrachloride, various tri- and tetra-choro ethanes and ethylenes, hexachlorobutadiene, di-, tri-, tetra-, penta-, and hexachloro-benzenes, etc. Since many of these are actual commercial products, it would be necessary that more than just a single intermediate be identified to support the like mechanism argument.

Magnesium and nickel refining

In one reference, the Battelle report states that there are indications of formation of both OCS and PCDD/F (Oheme et al. 1989) in magnesium and nickel refining. The authors also note that the processes result in the formation of hexachlorobenzene. Oheme et al. describe a unique PCDD/F fingerprint where the PCDF to PCDD ratio is 50:1. This would indicate that it is appropriate to suggest formation of OCS from a source if, and only if, the hexachlorobenzene was demonstrated to be present <u>and</u> the PCDF to PCDD ration was approximately 50:1. A more detailed examination of the PCDD/F fingerprint reported by Oheme et al. (1989) should be performed, and additional criteria should be considered (e.g., the 1,2,3,7,8-PeCDD to 2,3,7,8-TCDD ratio was 11:1). These criteria would provide a technical justification for assuming a like mechanism might be operative. At the same time, it should also be pointed out that the Oheme et al. work explicitly pointed out the vast differences between the Mg and Ni refining PCDD/F fingerprint and the fingerprint typically observed in incineration sources. This is explicit evidence that there is a completely different mechanism than the one responsible for the OCS from Mg and Ni refining that may be operative in incineration sources.

Other metal refining processes

Doring et al. (1992) describe the concurrent formation of OCS, HCB, pentachlorobenzene (PeCB), decachlorobiphenyl (DCB), and PCDD/F from a copper smelting process. Doring et al. (1992) describe conditions necessary for the formation of these compounds as follows:

> "A chlorine source is present (sodium chloride) and the reductive conditions transform Cl^{-} to Cl·-radicals. These are then able to chlorinate the aromatics formed by radical processes from the carbon source (coal) at the high process temperature."

They later note:

> "The chlorination roasting process of the copper slag has some similarities with the production of waterfree magnesium chloride (reductive conditions at high temperature (>700°C), presence of carbon and Cl-radicals)."

Much like the fingerprint for the above described Mg process, there is a clear predominance of PCDFs, with the PCDF/PCDD ratio at about 10:1.

This illustrates the importance of corroborating mechanistic hypotheses with confirmatory data. Only when clearly analogous conditions are observed and similar fingerprints are demonstrated (e.g., PCDF/PCDD ratio of 10:1, presence of HCB, DCB, and PeCB) can one reasonably infer the formation of OCS.

Perchloro solvent manufacturing

In the work reported by Pereira et al. (1988), which the Battelle report cites as evidence of a link between OCS and HCB, the authors also report the presence of high levels of di-, tri-, tetra-, and penta-chlorobenzenes, as well as hexachloro-1,3-butadiene and octachloronaphthalene as by-products of chlorinated solvent manufacturing. Thus, before invoking an argument that the presence of HCB is an indication of potential OCS via the same mechanism, evidence of these other co-contaminants that would support the hypothesis of a like formation mechanism should be provided. Otherwise, there is no justification for supposing a like mechanism.

To summarize, before any surrogate chemicals like PCDD/F or HCB can be used as indications of the potential for OCS formation, there should be some corroborative data which provides supporting evidence that a like reaction mechanism is operative. Without such evidence, the extrapolation from one source to others using the presence of these proposed indicator compounds is technically insupportable.

Chlor-alkali production

The Battelle report sites the work of Kaminsky and Hites (1984) as evidence of the formation of OCS in the chlor-alkali process where carbon electrodes are utilized. In work published by Rappe et al. (1990), a PCDD/F fingerprint for this type of process was shown to produce a large predominance of PCDFs. For instance, sludge from electrodes was found to contain 52,000 pg/g 2,3,7,8-TCDF vs. non-detectable levels of 2,3,7,8-TCDD. Similar high ratios were found for the higher homologues. Thus, inferring a relationship between known sources of PCDD/F from electrolytic processes and the potential for production of OCS would only be technically defensible if it were demonstrated that the PCDFs clearly dominated the fingerprint. If another fingerprint is observed, it would be sufficient evidence that an alternative mechanism is operative and that, in the absence of other evidence concerning that mechanism and its by-products, it would be inappropriate to infer the formation of OCS.

Reaction Conditions

Table 1 provides a partial summary of conditions where OCS has been demonstrated to form (as described in the Battelle report, not independently verified). All can be characterized as high energy processes. Some involve high electrical currents, some high temperatures, and some both. In many cases, Cl_2 gas or other chlorinated solvents are used to create certain atmospheres, and conditions are such that they are clearly intended to react. Characterization of other potential sources of OCS should include careful comparison of the conditions known to produce OCS and those of the candidate process.

Table 1.   Reaction Conditions of Known Sources of Octachlorostyrene

Process	Temperature	Energy Input	Carbon Source	Chlorine Source
Chlor-alkali	not specified	electric current	carbon electrodes	brine and Cl_2 produced
Mg refining	1000-1200°C	electrodes	carbon electrodes	Cl_2 atmosphere
Al degassing	600°C	unspecified, (sufficient to melt Al metal)	hexachloro-ethane	hexachloro-ethane or Cl_2
Cu smelting	700°C	unspecified, (sufficient to melt Cu metal)	coal	8% NaCl under reducing conditions
Secondary Pb smelting	1260°C	incineration	battery casings	PVC separators

Stoichiometry

Examination of the metals refining processes described in the Battelle report strongly indicates that in most cases there is excess chlorine relative to carbon (high chlorine to carbon ratio). This is also true for the production of carbon tetrachloride and tetrachloroethane. If one considers the chlor-alkali process, where a large volume of Cl_2 is produced from a comparatively small mass of carbon (in the form of the electrodes), there is also a high Cl/C ratio. Under these circumstances, it seems apparent that the potential for the formation of highly chlorinated compounds like OCS exists. However, it would

not be appropriate to assume that if the right temperature and/or other conditions were present, the same potential for formation of OCS exists where the ratio is the opposite.

To a certain extent, dilution may also be an important consideration. Reactions that proceed in high yield at high concentrations may not proceed at all if performed under dilute conditions.

Examples of the Use of These Principles

Pulp bleaching

A perfect example of the need to provide some supportive evidence of like mechanisms is the insupportable extrapolation of the historical presence of PCDD/F in pulp mill effluents and the suggested formation of OCS. It has been well established that the formation of PCDD/F in pulp bleaching was caused by electrophilic aromatic substitution of the unchlorinated dibenzo-p-dioxin and dibenzofuran (Kringstad et al. 1988; Voss et al. 1988; Berry et al. 1989; LaFleur et al. 1990). This type of ionic chemistry occurs because bleaching is performed in an aqueous environment. Free radical chemistry (as invoked by the Schulman and Klingele *de novo* formation hypothesis) is detrimental to the quality of the pulp; thus, steps are taken to suppress this chemistry. In older bleaching processes, this involved the use of 12 to 15% chlorine dioxide, a free radical scavenger. The active chlorinating agent responsible for the formation of PCDD/F in pulp bleaching is Cl_2. In order to eliminate the potential formation of PCDD/F in bleaching, the US and Canadian pulp and paper industry has moved to the use of chlorine dioxide bleaching processes. The switch to this bleaching chemistry has virtually eliminated all TCDD/F formation, and forms the basis of the NPDES effluent guideline limitation recently promulgated by EPA.

EPA conducted extensive sampling and monitoring of a variety of bleaching processes in the development of their effluent guideline (Federal Register 1998; US EPA 1993). This work included testing for many of the compounds that would provide evidence for other potential OCS mechanisms. Included in these analyses were carbon tetrachloride; tri- and tetra-chloro ethanes and ethylenes; di-, tri-, and hexachlorobenzenes; hexachlorobutadiene; and even styrene itself. EPA found no evidence of the presence of these compounds in the bleach plants they studied. This provides further evidence that the types of high energy free radical chemistry required to form OCS are simply not present in pulp bleaching.

To summarize:

The historical formation of PCDD/F in the bleaching process has been demonstrated to be due to an electrophilic aromatic substitution mechanism, <u>not</u> a high energy free radical mechanism.

Since free radical chemistry has undesirable effects on pulp quality, steps are taken to minimize it.

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The pulp industry has changed its bleaching practices to the point where TCDD/F formation is virtually eliminated. These process changes have significantly reduced the incidental formation of other chlorinated organics as well.

EPA's data generated during their development of the pulp and paper industry effluent guideline demonstrate the absence of other indicator compounds that should be present if the *de novo* OCS mechanism was operative.

Taken together, there is no justification for extrapolating from the historical presence of PCDD/F in pulp bleaching to the potential for this process to produce OCS. In fact, the clear understanding of the reaction mechanisms responsible for the presence of PCDD/F in historical bleaching processes is evidence that OCS would not be expected.

Vapor phase degreasing

The Battelle report seems to liken the process of vapor phase degreasing with aluminum degassing. In the case of the aluminum degassing process, the temperatures are above the melting point of aluminum (reported by Battelle as 600°C), and either hexachloroethane or chlorine gas are introduced to force their reaction with hydrogen. Comparing this with solid metal parts at or just below the boiling point of the solvent (e.g., 74°C for 1,1,1-trichloroethane) and inferring a potential for the formation of OCS is not technically sound.

Pesticide manufacture

The Battelle report sites pesticide manufacturing as a potential source of OCS. The discussion seems to involve mostly 2,4-dichlorophenol and products made using it as an intermediate. The process cited in the Battelle report is the controlled chlorination of phenol using a reasonably selective chlorination agent. There is nothing in this process that even begins to suggest the kinds of conditions necessary to produce OCS.

The authors state, "The methods for producing 2,4-dichlorophenol include the direct chlorination of phenol and/or monochlorinated phenol using chlorine or sulfuryl chloride (SO_2Cl_2) with chlorination promoters and stabilizers. In as much as this reaction is known to form CDD/CDFs, it is by analogy, suspected of forming OCS," citing Kirk-Othmer 1996. We have examined the Third Edition of the reference (which is the only edition we had ready access to), and find that the statement that "In as much as this reaction is known to produce CDD/CDFs…" is a very misleading interpretation. Kirk-Othmer noted that polychlorophenols are starting materials for the synthesis of PCDDs and use 2,4,5-trichlorophenol as the starting material for 2,3,7,8-TCDD. There is no indication that chlorination is the mechanism responsible. For a discussion of the currently accepted mechanism for PCDD formation in chlorophenol manufacturing, see the following discussion on pentachlorophenol. Other workers (e.g., Firestone et al. 1972) have analyzed technical formulations of dichlorophenolics and found no dioxin contamination.

Pentachlorophenol (PCP) production

Generally, the incidental formation of PCDDs during pentachlorophenol manufacturing is thought to be due to the strong basic conditions and condensation of the chlorophenolate salts with each other (see US EPA 1980 for discussion of reaction mechanism). The initial condensation forms a polychlorodiphenyl ether, which then undergoes an intra-molecular reaction to form polychloro-p-dibenzodioxin. Since technical pentachlorophenol has significant levels of tetrachlorophenols, the PCDD distribution is predominated by OCDD, followed by varying amounts of HpCDD and HxCDD. Generally, PCDFs are at much lower levels. It is also notable that polychlorohydroxydiphenyl ethers are co-contaminants of PCP (Jensen and Renberg 1972; Jensen and Renberg 1973; Nilsson et al. 1974). This fingerprint or product distribution does not resemble any product distribution associated with known sources of OCS. There is no similarity in the reactions responsible for PCDD formation in PCP manufacturing (which are largely ionic) and the *de novo* high energy free radical chlorination and coupling reaction described by Schulman and Klingele (1985). There is no indication that any of the other OCS precursors are present. Thus, no evidence has been presented or is available indicating that there is any similarity to the mechanism for PCDD formation in pentachlorophenol and any known mechanism for OCS formation.

Estimating an OCS Inventory Based on the Presence of PCDD/F

The Battelle report outlines a series of assumptions around ratios of HCB, PCDD/F, and OCS to develop emission factors, then uses the Oheme et al. (1989) sediment data to develop a numerical ratio for extrapolating PCDD/F data to predict or inventory other OCS sources. As was discussed previously, the fingerprint from the metals refining process studied by Oheme et al. (1989) was specifically noted by the authors to be unique. This is actually data that indicate that one should <u>not</u> use this as the basis of a conversion factor for any source other than other metal refining processes, or perhaps the chlor-alkali process, since it clearly demonstrates that this source is unique. Until a link has been established between OCS and a given mechanism of PCDD/F formation, it is totally inappropriate and counterproductive to the goals of the Binational Toxics Strategy to generate "generic" PCDD/F-to-OCS emission factors to estimate source emissions or to develop an OCS inventory. Thus the entire rationale used in Section 4.2 to establish a cornerstone for developing an OCS source inventory is fatally flawed and should be discarded.

Fate Based OCS Release Rate Estimation

Mr. Robert Bailey has reviewed the premise put forth in the second Battelle report regarding the calculation of OCS/HCB/Dioxin ratios from sediments, and their application to suspected source generation rates. He has found this presentation to be seriously flawed. Estimates of OCS releases to the Great Lakes Basin have been grossly over estimated.   His comment follow.

As the Battelle authors found when attempting to compile a report on sources of octachlorostyrene (OCS), there is essentially no direct information available on production and releases of OCS. Their approach was to summarize what information they found on the occurrence of OCS in the environment and potential sources. However, there was no segregation of the data by time so that the conclusions are based in large part on older information, reflecting technology and practices from the 1970s and earlier. In addition surrogates were incorrectly used to estimate OCS emissions and concentrations in the environment. **The conclusion that OCS may be currently, 1999, emitted in significant quantity in the Great Lakes region is not supported by the available data.** The reported dramatic decreases in most of the observed concentrations over the past 30 years and concurrent and continuing decreases in related chemicals suggest that OCS may be disappearing from sight in the Great Lakes.

Environmental Concentrations

In the Great Lakes and elsewhere the observation of OCS in the environment has been the clue to production and release of OCS from a variety of industrial processes. Sediment cores in Lake Ontario show a peak in the concentration of many chlorinated chemicals, chlorobenzenes, pesticides and OCS around 1960 (Kaminsky and Hites, 1984, Durham and Oliver, 1983)[2]. Since that time, waste disposal as well as production technology have improved with great reductions in the release of these chemicals to the environment. In fact, already by 1981 Durham and Oliver (1983) reported the concentration of OCS in Lake Ontario sediments had dropped by over 95% from its 1960 concentration. Huestis et al. (1996) report an approximately 90% decrease in the concentrations of both OCS and HCB in fish from Lake Ontario between 1977 and 1993. The concentration of OCS in Niagara River suspended sediments has continued to drop during the period of 1990 through 1995 (Niagara River TMP).

Sources of OCS

The major recent (post-1980) sources of OCS in the environment seem to have been landfills which received waste from the old processes (pre-1980) described in the Battelle report. For example, prior to the 1970s landfill in the Niagara Falls area received "taffy tar" containing OCS and many other chlorinated organics from the production of chlorine. However the release of OCS from these old landfills has been and will continue to be reduced by (a) cleaning old storm sewers of accumulated chemicals and (b) diverting the current landfill leachate from the landfills to wastewater treatment (Niagara River TMP). This storm sewer cleaning and landfill leachate diversion to wastewater treatment has been and is an ongoing part of the cleanup of the Niagara River.

A second example of reduced OCS emissions is the cleanup of the Ashtabula River. Emissions of OCS and other chlorinated chemicals into the Ashtabula River have been

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[2] For complete description of references see bibliography contained in Appendix II

essentially eliminated and a dredging program is planned to remove contaminated sediments which could spread into Lake Erie (Mahan, 1999).

The formation of trace levels of OCS has been documented for a number of processes where chlorine and carbon are present at high temperatures or in electrochemical reactions (Vogelsang, 1986; Kaminsky and Hites, 1984). In general these processes have not been studied closely for OCS because of its low concentrations. As suggested by Schulman and Klingele, it is logical to attempt to predict OCS emissions from the HCB or PCDD/Fs emissions from a variety of processes. The formation of OCS along with HCB, hexachlorobutadiene and polychlorodioxins and furans (PCDD/Fs) from the successive accumulation of two-carbon units, as proposed by Schulman and Klingele, is easy to accept based on the pyrolysis experiments of Lahaniatis (1989). Similarly, the pyrolysis of hexachloroethane used in degassing of molten aluminum in laboratory experiments by Westberg et al. (1997) and qualitatively confirmed by Vogelsang (1986) is consistent with Schulman and Klingele's proposal. However, the formation of PCDD/Fs seems to have a large surface catalysis component which varies widely under different conditions and may be different for OCS. The variations reported in the mixtures of PCDD/Fs from different processes also introduce a great deal of uncertainty in the ratio of OCS production to that of PCDD/Fs. (Summing the different congeners based on their toxicity to calculate a TEQ adds another layer of uncertainty). HCB is chemically more like OCS so that it may be a better surrogate for estimation of OCS concentrations in the environment. However, neither HCB nor TEQ can be considered a good surrogate for OCS in the absence of information linking OCS to each of the wide variety of processes considered in the Battelle report.

In addition, HCB is formed as a byproduct in some specific reactions in the production of highly chlorinated pesticides such as dimethyl tetrachloroterephthalate. Thus, the use of surrogates such as HCB, in the absence of specific information on emission ratios, must be used for only preliminary, order of magnitude, estimates of OCS emissions. Differences in the environmental degradation rates of OCS and surrogates could also change the observed ratio, especially in old samples, and not enough information is available at present to confidently assign the expected change in ratio.

Estimates of OCS emissions from HCB and PCDD/Fs were made in the Battelle report. However, this author will outline below several defects in the Battelle report's estimates of OCS emissions. The first error was taking the relative concentrations of OCS and HCB in sediments as reflecting their water concentrations without correcting for their different partition coefficients. Also, the Battelle report based its ratio of OCS to TEQ (PCDD/F) solely on data from a study of one river, the Elbe. This author proposes using an alternative study based on 400 sites in the U. S. (Kuehl and Butterworth, 1994).

The use of HCB concentrations in environmental samples as a measure of OCS needs to take into account their different physical properties which affect their partitioning in the environment. Neutral chemicals adsorb on sediments in proportion to their octanol/water partition coefficient, Kow (Karikoff et. al., 1979). The log Kow of OCS is estimated to be

approximately 7.46 from structure activity correlations (SRC online Kow) and the log Kow of HCB, approximately 5.5 (Mackay et. al., 1992). Thus, OCS is estimated to adsorb about 100 times more strongly on sediments than HCB. That is, the concentration of OCS on sediment would be 100 times that of HCB at equal water concentrations.

The OCS/HCB sediment concentration ratio for some sediments are:

Durham and Oliver (1983)   0.15, mean, 1900-1981, Lake Ontario
Oliver and Bourbonniere (1985) 0.11, mean, 1980, 1982, Lakes Huron, Erie
Krieg and Krausch (1993)   0.15, mean, 1985-87, Elbe Estuary
Drouilliard et al. (1996)   0.26, mean, 1996, Detroit River

Thus, the concentration of OCS is estimated to be between 0.01 and 0.001 of that of HCB in the water. Presumably, the relative concentrations of OCS and HCB originally emitted would therefore also be between 0.01 and 0.001.

Atmospheric concentration measurements of OCS and HCB are likely to represent current emission ratios. However, such measurements have not been carried out extensively. Hoff et al. (1992) reported atmospheric measurements of OCS and HCB in 1988-89 in Canada near the shore of Lake Ontario. Unfortunately due to experimental design error, their sampling system did not collect all of the HCB during the summer but still the mean concentrations of HCB were nearly 100 times those of OCS, 54 vs. 0.71 pg/m^3. More recent measurements by Dan et al. (1999) did not detect OCS most of the time. HCB is included in the suite of compounds being regularly monitored in the International Atmospheric Deposition Network (IADN) program in the Great Lakes. Results from this program generally show a substantial and steady decline in atmospheric concentrations of HCB and other chlorinated chemicals since 1991 (Cortes et al., 1998, Hillery et al., 1997).

A factor for estimating the environmental concentration of OCS relative to that of 2,3,7,8-TCDD can be derived from the work of Kuehl and Butterworth (1996) in their survey of fish from nearly 400 sites throughout the United States. They report a mean concentration of 2,3,7,8-TCDD in fish of 13.6 pg/g, which made up 55% of the TEQ and a mean of 1.7 ng/g OCS. Converting the mean TCDD concentration to TEQ gives 25 pg/g TEQ which yields an OCS/TEQ ratio of 1700/25 or 68. Correcting for the increased bioaccumulation factor of OCS, $117x10^6$, vs. TCDD, $9x10^6$ (Battelle report) suggests a concentration factor of 68/(9/117) or OCS = 5.2 TEQ. Using this procedure, the concentration of OCS in the environment, and presumably emissions, would be five times the TEQ concentration. This factor can be compared with the OCS/TEQ factor of 653 used in the Battelle report which was derived from data in the Elbe River. The large number of non-detected OCS concentrations which were included at half the detection limit in the study by Kuehl and Butterworth lead to some uncertainty in the factor of five but this uncertainty is probably less than the overall uncertainty in using such a surrogate for OCS as TEQ.

Larry LaFleur has shown that the one-size-fits-all approach used by Battelle to suggest OCS sources is flawed. Additionally, the errors discussed above in the procedure which they used to establish their ration factors produce erroneous release rate figures. Going

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through Table 4 of the Battelle report applying a multiplier of 5 to the dioxin emissions and 0.01 to the HCB emissions yields a different perspective on OCS emissions, about 60 pounds OCS emissions for the entire U. S. versus the 4000 pounds estimated in the Battelle report. Mr. Dan Smith has reviewed OCS levels in the environment and concluded that air deposition is not a significant input vector for the Great Lakes. (See discussion which follows.) Given this finding, out-of-basin sources must be discounted from the 60 pound figure. Once the correct analytical data is used to determine if a source or sector actually releases OCS (or a properly identified and ratioed surrogate), the proper surrogate ratio is identified and applied, the "source" is only included if it is in the Great Lakes Basin, and the continuing operation of the "source" is confirmed, the actual Great Lakes Basin OCS release numbers will be substantially lower, and probably not significant.

The Status and Trends of OCS in the Environment

To confirm the lack of significance of the potential or suggested OCS sources which may remain in the Great Lakes Basin, a review of the status of OCS levels in the environment has been made by Dr. Dan Smith of Conestoga Rovers Consulting. The following analyses reviews his findings regarding the current status and spatial and temporal trends of octachlorostyrene (OCS) in Great Lakes media. These questions were addressed:

- What are current concentrations of OCS in Great Lakes media?
- How have concentrations changed over time?
- How do concentrations vary from place to place?
- What can be deduced concerning current sources and future trends?

Methods: Data on OCS concentrations in Great Lakes media were collected from available sources. Emphasis was placed on analyses of data sets that were extensive and relatively consistent in terms of methods of collection and chemical analyses. While some of the data have been published, most recent data were sought and obtained from various agencies. The Canadian Wildlife Services (CWS) supplied more recent data from that agencies long range monitoring of colonial bird eggs.   The Ontario MOE supplied recent data on OCS concentrations spottail shiners from the Niagara River. Unpublished data from MOE's monitoring of water and suspended solids in the St. Clair and Niagara Rivers were obtained from MOE. The USEPA supplied unpublished data on OCS concentrations in Lake Ontario, collected by the EPA.

Temporal trends were analyzed based on the model of first order decline

$$C_t = C_0 * \exp^{(rt)}$$

Where C_t is the concentration at time t, C_0 is the concentration time 0 or the start, and r is the first-order rate constant. First-order decline assumes that proportional rates of decline are constant over time, that is

$$\frac{dC}{C\,dt} = \text{constant}$$

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First order decline is the most appropriate model for decline of persistent chemicals in the environment because the fate processes that reduce ambient concentrations (e.g., burial, biodegradation, volatilization, photolysis, and dilution) are themselves first order processes. Because temporal trends are assumed to follow first order kinetics, temporal trends were tested with linear regression analysis after transforming concentrations to the natural logs. This produces the following equation

$$Ln\ (C_t) = Ln\ (C_0) + r * t$$

In which all parameters are the same as in the first equation. The existence of a first order decline can then be tested, statistically, with linear regression of log concentration on time of collection. Logarithmic transformation of concentration also tended to normalize residuals, a requisite for the use of parametric statistics.

Because absolute changes in concentrations fall as concentrations fall, first order reactions will always trace a concave up path when plotted on the usual linear XY graph (Figure 1)[3]. The inevitable concave up shape, unfortunately, misleads many viewers into believing that concentrations of orgaonchlorines (OCs) are stabilizing over time. Thus, all temporal trends will be depicted on the semilog scale. Time is plotted on the linear X-axis while untransformed concentrations are plotted on a logarithmic Y-axis (Figure 2). Readers unfamiliar with the semilog scale should be advised of the following. First, equal distances on the logarithmic Y-axis represent equal percentage changes in concentration. Consequently first order declines now trace a straight line (Figure 2), eliminating the optical illusion of stabilization that occurs on the linear XY plot. Secondly, absolute changes in concentration tend to look smaller than when plotted on the linear Y-axis, as shown in Figures 1 and 2. When assessing progress over time, therefore, it is important for the reader to look closely at the Y-axis.

Because percent declines per year are more accessible than first-order rate constants, rates of decline over time will be described in the text below in terms of percent declines as opposed to the first order rate constants produced by the regression analyses.

Results

Gull Eggs from the Great Lakes

The CWS eggs sampling program is the best available data base for determining status and trends of organochlorines in the Great Lakes. Since the early 1970s, CWS has assessed OC concentrations in gull eggs from a number of colonies across the Great Lakes. The positions of the colonies are depicted in Figure 3. The gull egg data are extensive over time and space and have benefited from a relatively consistent sampling and analytical methodology (described in Bishop et al. 1992 and Petit et al. 1994)[4]. Another advantage

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[3] Figures appear in Appendix III.
[4] For complete reference citations see bibliography in Appendix IV.

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of the gull egg data is that the data are regularly disseminated and available to the Great Lakes research community. Thus, the strengths and limitations of these data are better understood than other Great Lakes data sets (e.g., see Smith 1995a, Stow 1995, Hebert et al. 1996, Hebert et al. 1998).

These data were statistically analyzed (by colony and by Great Lake grouping) to determine whether trends were statistically significant. OCS in herring gull eggs declined significantly ($p < 0.05$) from 1987 to 1998 in eggs from all colonies except three – Leslie Spit and Snake Island on Lake Ontario, and Chantry Island on Lake Huron (Figure 4). In the latter three cases, the regressions were marginally significant (e.g, $p < 0.10$). Moreover, when the data from all colonies on a Great Lake were grouped together, rates of decline are highly significant for each Great Lake.

On average, OCS concentrations in gull eggs from colonies on Lakes Erie, Huron, and Ontario tended to be higher than those from Michigan and Superior (Figure 5), although there was considerable variability between colonies on the same Great Lake (Figure 6). OCS concentrations were only sometimes elevated in gull eggs taken from colonies near historical sources such as Channel Shelter Island on Saginaw Bay, the Fighting Island Colony on the Detroit River, and the colonies on Lake Ontario. On the other hand, OCS concentration from the Port Colborne colony on the eastern Basin of Lake Erie and the Niagara River colony were both quite low despite their proximity to historical sources in the Ashtabula and Niagara Rivers (Battelle 1998). The rates of OCS decline over time among lakes were remarkably consistent, despite intralake variability. By colony, rates of decline varied from about 9% per year at Channel Shelter Island to about 24% per year (Figure 7), both on Lake Huron. However, the rates of decline were not significantly different (ANCOVA, $p > 0.05$) across all Great Lakes colonies, and all colonies tended to decline at an average rate of 18% per year. Concentrations of OCS in most colonies are approaching the detection limit (about 1 ppb) (Figures 5 and 6). Eggs were below the limit of detection at least once between 1995 and 1996 in all colonies except two – the Middle Island colony in Lake Erie and the Channel Shelter Island colony in Lake Huron.

Conclusion: From 1987 to 1998, concentrations of OCS in gull eggs fell significantly and somewhat rapidly, on average about 18% per year (Table 3). The rates of decline did not differ statistically among colonies, and declines were very uniform across lakes and connecting channels. These decreases have reduced the concentrations of many colonies to levels near the limit of detection. Spatially, colonies from Lakes Ontario, Erie, and Huron have similar concentrations. Concentrations of OCS in gull eggs from colonies on Lake Superior and Michigan are similar to each other but lower than from the other Lakes.

Spottail Shiners from the Niagara River and Lake Ontario.

Another very useful long-term database for OC in the Great Lakes is provided by spottail shiners represent These data are the property of the OMOE and the Canadian Government, ana collection and analytical methods are described in Suns et al. (1982, 1993) and Suns and Hitchin (1992). As with the gull-egg data, the spottail-shiner data

benefit from relatively consistent methods over the long term as well as frequent sampling over time and space. However, only the data from the Niagara River were obtainable for this report. OCS concentrations in spottail shiners from the upper Niagara River are only rarely above the detection limit, making temporal trends analyses impossible. However, OCS concentrations in shiners from the lower Niagara River were generally above the limit of detection in the beginning of the sampling period in the mid-1980. When less than detect values are assigned the value of ½ the detection limit, OCS concentrations in the lower Niagara River are estimated to have fallen about 8% per year (p < 0.05, Figure 7).

Conclusions: Concentrations in shiners taken from the lower Niagara declined at about 8% per year, falling from about 4 ug/kg in the mid 1980s to less than detection in the mid 1990's.

Lake Trout from Lake Ontario

The Canadian Department of Fisheries and Oceans (F&O) collects lake trout and smelt from each of the Great Lakes on an annual basis. F&O data are not readily available to the public or Great Lakes scientific community, so the quality, methods, and extent of these data could not be ascertained. According to information presented in Huestis et al. (1996), lake trout samples from Lake Ontario are analyzed for OCS. These data show significant (P < 0.05) declines, about 10% per year, in OCS over time in Lake Ontario lake trout.

Conclusion. Concentrations of OCS fell significantly, about 10% per year, in Lake Ontario lake trout from 1977 to 1993.

Figure 5. Best-fit declines of OCS in herring gull eggs grouped by Lake and Connecting Channel.

Water and Suspended Sediments from the Niagara River

The Upstream/Downstream monitoring group samples water at the beginning and end of the Niagara River, at Fort Erie and Niagara-on-the-Lake. These data, therefore, provide information on water quality conditions in Lake Erie, the Niagara River, as well as information about loading of OCS to Lake Ontario. This is a high quality database with relatively consistent methods over time and very frequent sampling. These data are also regularly published and easily obtainable by the Great Lakes science community.

OCS data were obtained from the Upstream/Downstream sampling group for the period between 1989 and 1995. During this period, water samples were generally taken every week. Whole water samples were divided into aqueous and suspended sediments, and chemical analyses were conducted on these two fractions. Although there are MDLs reported for both fractions -- 0.05 ng/l for the aqueous fraction and 2.7 ng/g of suspended sediment -- concentrations well below the MDL (20% or less of the MDL) are routinely reported. Thus, these reports produce three types of data: estimated concentrations above

the MDL, estimated concentrations below the MDL, and data listed as below the detection limit.

At Fort Erie, at the origin of the Niagara River, 281 aqueous fractions and 285 sediment fractions were analyses[5]. None had a reportable concentration of OCS. Thus, OCS was never detected in 566 analyses representing about 285 water samples. OCS was detected at the mouth of the Niagara River at Niagara-on-the-Lake. For the aqueous fraction, 270 analyses were conducted. Concentrations for the aqueous fraction were 43 times between 1989 and 1991, but not since then. For the adsorbed fraction, reportable concentrations of OCS were detected more frequently concentrations, about 55% of the time. To determine long-term trends, total water concentration of OCS for each sample was estimated in the following manner

$$[OCS]total\ water = [OCS]aqueous + [OCS]adsorbed * [suspended\ solids].$$

Given the large number of analyses below detection, the results of a trends analysis will depend somewhat upon what values are given to unreported values. To insure that trends were real, various values were given to the unreported values for adsorbed OCS: 1/2 the detection limit (1.35 ng/g), 1.0 ng/g, and 0.37 ng/g, the lowest value reported. OCS was rarely reported in the aqueous fraction, so unreported data in the aqueous fraction were set equal to zero.

No matter how non-reported values were treated, OCS concentrations were estimated to have fallen significantly over the period. However, the estimated rate of decrease was dependent upon what values were used for unreported values. OCS concentrations declined by about 40% per year when unreported values were set equal to 0.37 ng/l, but only about 28% per year when unreported values were set equal to 1.35 ng/g, one half the detection limit (Figure 8). Ignoring the aqueous fraction and setting unreported values equal to 1.35 ng/g, OCS concentrations on suspended sediments fell about 21% per year. These analyses demonstrate that OCS concentrations really did decline over this period. However, detecting future declines will become more difficult as more and more analyses yield values below the reporting level.

All of these measured rates of decline are probably faster than the long-term average. Oliver and Charlton measured OCS in the Niagara River several times in the fall of 1982. They found an average OCS concentration of 0.06 ng/l in whole water, which is approximately three times the geometric mean concentrations found in 1989. These two dates trace a 15% per year decline. Similarly, OCS concentrations in the Niagara Bar (discussed below) demonstrate long-term declines of about 14.5% per year.

Conclusion. From 1987 to 1995, OCS concentrations at Fort Erie were always lower than the detection limit in both water and suspended sediments. At Niagara-on-the-Lake

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[5] The number of aqueous data points does not equal the number of suspended sediment data point because data for one or the other medium are sometimes, albeit infrequently, rejected because of QA problems.

at the mouth of the Niagara River, OCS was detected at reportable concentrations on a semi-regular basis, especially adsorbed to suspended sediments. OCS concentrations in whole water and suspended sediments fell rapidly over this period, between 21% to 40% per year, depending upon the value applied to unreported values. Based on these data, loading of OCS to Lake Ontario is estimated to have decreased about 70% or more between 1989 and 1995.

Suspended sediments and water from the St. Clair River

MOE monitors water at two points in the St. Clair River, Port Edward at the beginning of the of the St. Clair River and downstream at Port Lambton. The methods are similar to those used in the Upstream/Downstream sampling: sampling on a frequent basis (every two to three weeks), fractionation into an aqueous and sediment fraction, detection limits of 0.05 ng/l and 2.7 ng/g, respectively, and analysts who routinely report concentrations below the detection limit. Of 103 analyses of the aqueous fraction sampled at Port Edward between 1987 and 1996, only 5 samples had reportable concentrations of OCS. These 5 samples averaged 0.02 ng/l OCS. Only two of 111 analyses of suspended sediments had reportable concentrations of OCS.

Reportable concentrations were more frequent downstream at Port Lambton. Of 141 analyses of the aqueous fraction taken between 1987 and 1994, only 7 had reportable concentrations of OCS. However, OCS was regularly reported adsorbed to particles. About 90% of analyses of suspended sediment yielded reportable concentrations of OCS (Figure 9). When unreported concentrations are set equal to one half the detection limit, these data produce a significant decline of about 15% per year.

Conclusions: OCS concentrations have generally been well below the limit of detection at Port Edward at the origin of the St. Clair River. Downstream at Port Lambton, OCS concentrations dissolved in water are also infrequently detected above the detection limit. However, concentrations adsorbed to suspended sediments are generally at reportable concentratons, although these concentrations appear to be falling at about 15% per year over the last decade.

Data for the St. Lawrence River/Outflow from the Lake Ontario

Environment Canada also samples OCS at the origin of the St. Lawrence River. These data are diagnostic of St. Lawrence conditions as well as Lake Ontario. The data are apparently generated using the same general methods as with Niagara River and St. Clair River sampling. Reported detection limits were 0.07 ng/l for water and 2.7 ng/g for the adsorbed fraction. For 85 samples taken from 1989 to 1994, OCS concentrations were reported once in the water column and 11 times in the suspended sediment fraction. All of the reported concentrations were below the detection limits. The eleven concentrations reported for the sediment fraction 0.9 ng/g. The single value reported for the aqueous fraction was 0.01 ng/l, which is 1/7th the MDL.

Conclusion. Concentrations of OCS in the headwaters of the St. Lawrence River/outflow of Lake Ontario are infrequently detected at concentrations that can be estimated. Current concentrations are well below the detection limit.

Bottom Sediments from Lake Ontario

Two sediment core samples have been taken from Lake Ontario and analyzed for OCS. Durham and Oliver (1983) took a sediment core in the Niagara Bar in 1981, and core samples from the Niagara Bar were taken in 1995 by New York Department of Environmental Conservation (NYDEC 1996). The two cores showed a consistent pattern (Figure 9). In both cores, OCS concentrations in sediments apparently peaked about 1960 and then declined at about 13.5%.per year (Figure 10). For the NYDEC sample, OCS concentrations in sediments deposited after about 1981 were always below the detection limit, which ranged from about 13 to 6.4 ug/kg.

The yearly declines estimated between 1960 and 1981, when OCS concentrations were above the detection limit, can be extrapolated to the present. Assuming that past rates of decline continued to the present, OCS concentrations in Niagara Bay sediments in the early 1990s should be between 0.5 and 1.0 ug/kg (Figure 8). This projection can be compared to the sediment trap data from the Niagara Bar (Oliver and Charlton 1988) and suspended sediment data from the Upstream Downstream Monitoring of the Niagara River (see section above on the Water Concentrations in the Niagara River). Sediments captured in sediment traps should reflect sediments being laid down during that period. Similarly, OCS concentrations in sediments deposited in the Niagara Bar should be a function of OCS concentrations on suspended sediments at the mouth of the Niagara River, which is the source of most particles settling onto the Niagara Bar.

In both cases, however, concentrations of settling and suspended sediment must be normalized to organic carbon levels similar to those found in bottom sediments to reflect the reduced binding capacity of coarser, less organic sediments that finally settle onto the Niagara Bar. Most recently deposited Niagara Bar sediments are about 3.1% organic carbon (NYDEC 1996). Organic carbon concentrations found in sediment traps were about twice those found in settled sediments (Oliver and Charlton 1988). Thus, sediment trap concentrations were divided by two to normalize for organic carbon (Figure 10). The concentrations measured by Oliver and Charlton fall very near the extrapolation line.

The fraction of organic carbon in Niagara River suspended sediments varies considerably, ranging between about 5% to over 30% organic carbon (Kuntz 1988)[6]. Assuming a geometric mean concentration of 10% would require a correction factor of 3.2 to normalize the suspended sediment to the 3.1% organic carbon of the deposited sediments. When concentrations of OCS on suspended sediments from the mouth of the Niagara River are divided by this correction factor, most recent suspended sediment concentrations

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[6] These data were kindly supplied by J. Merriman, Ecosystem Health Division of the MOE.

also fit right on the extrapolation line (Figure 10). This combination of information suggests that OCS loading to Lake Ontario has continued to fall at about the same rate (about 14.5% per year) from 1960 to the present.

Conclusion: As evidenced by OCS concentrations in Niagara Bar sediments, loading of OCS to Lake Ontario apparently peaked in the early 1960s, and has fallen about 14.5 % per year since that time to the early 1980s. when concentrations became too low to be detected. More recent data on settling particles in the Niagara Bar region and suspended sediments in the Niagara River have concentrations similar to those extrapolated from the long-term trends, suggesting that this rate of decline has continued to the present.

Additional Data on Status and Trends. OCS was measured in Lake Ontario water column twice, in 1984 (Oliver and Niimi 1988) and 1996 (EPA, unpublished data). Both samples were taken during spring overturn in open water areas of the Lake and were replicated at several sampling locations. Oliver and Niimi report a mean OCS concentration of 4.7 pg/l in the aqueous phase. For the 1996 EPA sampling, all samples yielded concentrations below the detection limit: roughly 0.5 pg/l in the aqueous phase and 0.2 pg/l in the adsorbed phase. As OCS was not detected in any of the 4 samples (three stations with one station duplicated), it can be assumed that the real OCS concentration was well below the detection limit. A reasonable assumption is that the concentration was ½ the detection limits, or about 0.25 pg/l. Using these two dates only, there was about a 95% decrease in water column concentrations of OCS, or about 22% per year. This observation should be treated with caution. Only two periods were sampled, and the analyses were conducted by different analysts.

Discussion.

The above analysis was limited to straightforward description of observable status and trends of OCS in Great Lakes media. These analyses addressed basic questions of how OCS concentrations have varied in time and space. In the context of the "virtual elimination strategy", there is also the less straightforward question of what spatial and temporal trends really mean. Specifically, can spatial and temporal trends in measured concentrations be used as an indicator of underlying trends in external loading?

The simple answer to this question is "no." The problem with inferring changes in loading from changes in ambient concentrations is twofold. First, measured concentrations in many media are often not good indicators of in-lake inventories, especially when measurements are limited. Second, for systems at non-steady-state with external loading, trends of in-lake inventories may be based largely upon internal fate processes and have little or nothing to do with trends in external loading (Endicott et al. 1992a,b, Smith , under review.) With respect to the first problem, concentrations of organochlorines in biota (lake trout, gull eggs, spottail shiners) are known to respond to a number of other factors in addition to abiotic concentrations and levels of external loading. These factors, which confound interpretation of observed trends, include winter weather, prey availability, aquatic prey chain length and structure, terrestrial vs. aquatic foraging,

limnological factors, and potential effects of inter-lake migration (Rasmussen et al. 1990, Rowan and Rassmussen 1992,; Smith 1995a,b, under review; Hebert et al. 1995; 1998) Concentrations of chemicals in the water column and sediments are confounded by sampling error and actual variability due to storms and mixing events as well as long-term changes in lake trophy and suspended sediments concentrations.

In view of the confounding factors affecting organochlorine concentrations, caution should be exercised when extrapolating observed trends, over time and space, in any of the media above to underlying trends in in-lake inventories, and from there, to trends in external loading. This is especially true of inferences based on small data sets and short time trends. For example, consider the OCS data for gull eggs from Lake Ontario (Figure 11). The long-term trend from 1987 to 1998, which shows a significant decrease in OCS concentrations over time, actually consists of three short-term trends: concentrations tended to remain constant from 1987 to 1993, fell precipitously, about 90%, from 1993 to 1995, and then rebounded somewhat from 1995 to 1998 (Figure 11).

Several factors suggest that none of these short term trends is responding to underlying changes of in-lake inventories levels or external loading of OCS. For example, the initial period of stable concentration is more likely attributable to one of the confounding factors affecting organochlorine concentrations in gull eggs (e.g., food chain effects and/or the weather effect). This is apparent because most of the organochlorines also show stable concentrations from the period 1987 to 1993 (Smith 1995a). The organochlorines have disparate sources of external loading to Lake Ontario, and it is not reasonable to expect that the loading of the different external sources of different organochlorines would be synchronized. The short-term pattern of stable OCS concentrations in gull eggs is also inconsistent with data from Niagara River loading. The Niagara River should be the primary external source of OCS to Lake Ontario. Loading of OCS from the Niagara River declined rapidly, from 70 to 80% at the same time that gull egg concentrations remained constant (Figure 8 vs. Figure 11). With respect to the precipitous decline of OCS concentrations from 93 to 95, it is highly unlikely for OCS inventories in Lake Ontario to fall much more than 10% per year, even under condition of complete zero loading (e.g., see Endicott et al. 1992a).

On the other hand, more reliable indicators of trends in ecosystem inventories, but not necessarily external loading, can be obtained by focussing on long-term trends and by looking for similar trends among different media. Despite potential problems with any one data set, there is a high degree of certainty that OCS concentrations have really been falling over the period from 1980 to at least the mid-1990s in Lake Ontario. As summarized in Table 3, there are statistically significant and quantitatively substantial declines in all of the following media:

> inflowing Niagara River water concentrations (1989 to 1994)
> spottail shiners residing in that inflowing water
> in-lake water column concentrations (1994 to 1996, two dates only)
> gull eggs (1987 to 1998)

> lake trout (1977-1993)
> in-lake sediments (1960 to 1981 or 1994 if suspended sediment data can be included).

Similarly, we can be reasonably certain that OCS concentrations in the St. Clair River/Detroit River are also actually declining, because OCS concentrations are declining in the water column, gull eggs. Data on temporal trends in other Great Lakes areas are mostly limited to gull eggs. This might be problematic, except that OCS levels are falling at all of these other colonies, suggesting that OCS inventories are indeed declining in the Great Lakes. Equally important, Lake Ontario and the St. Clair/Detroit River are two of the three areas in which OCS levels are elevated. With the exception of Saginaw Bay, where OCS is also elevated in gull eggs, temporal trends in other Great Lakes areas are of less importance because levels in most media are already near or at the detection limit.

Keeping in mind the limitations of the data, the following addresses the questions posed at the beginning of this discussion.

- **What are current levels of OCS in Great Lakes media?**

As shown in Table 2, current levels of OCS in most media are now at the limit of detection or rapidly approaching this limit at most sites in the Great Lakes. The notable exceptions to this are OCS concentrations in lake trout in Lake Ontario. Extrapolating past rates of decline (about 10% per year) onto early 1990's concentrations (about 30 ug/kg in whole raw lake trout) suggest that whole raw lake trout will continue to exceed the current detection limit (1ppb) till about 2025. It is also likely that OCS is above the detection limit in fish from the other Great Lakes, and potentially the St. Clair/Detroit River and Niagara River. Assuming a relatively constant relationship between gull eggs and fish, it is likely that OCS would be about as high in Lake Erie and Lake Huron fish as in Lake Ontario. OCS might also be detectable in very large lake trout from Lake Superior and Lake Michigan.

- **How have levels changed over time?**

In all media with adequate data, levels of OCS are decreasing significantly and, compared to other organochlorines, relatively rapidly, e.g., 8% to 30% per year (Table 3). Rates of decrease over time are generally highly statistically significant, quantitatively substantial, and consistent across media, time, and space. It can be concluded with a high degree of certainty that OCS concentrations in the Great Lakes have declined dramatically over the last two decades.

- **How do concentrations vary over space, i.e., from place to place?**

Gull egg data suggest that OCS burdens in Lake Huron, Lake Erie, and Lake Ontario are higher than in Lakes Superior and Michigan, although there is substantial intra-lake variability between colonies from Lake Erie and Huron. Elevated concentrations appear

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to be related to historical sources in Saginaw Bay, the St. Clair River, and Lake Ontario. Data from other media are limited, but tend to support the spatial trends found in gull eggs.

- **What can be deduced concerning current sources and future trends?**

The available data suggest that atmospheric sources were probably never an important source of OCS to Great Lakes ecosystems. Gull eggs colonies with elevated concentrations are generally downstream of historical sources of OCS in Saginaw Bay, the St. Clair River, and the Niagara River. Concentrations of OCS in gull eggs from colonies on Lake Michigan and Lake Superior, which are far away from historical sources, tend to be about about 3 to 4 times lower than those downstream of suspected historical sources. It is also important to note that concentrations of OCS in gull eggs from all of the colonies are fallin at about the same rate in all Lake groupings (Figure 5). This observation is inconsistent with the hypothesis of significant current atmospheric inputs, as one would expect atmospheric dependent sites to decline at a different rate than colonies primarily affected by past and current riverine and point sources. The rapid decreases in OCS concentration in gull eggs and the other media also suggest that current atmospheric loading is relatively insignificant and allows unimpeded declines of OCS in the lakes. Consistent with all of these observations, OCS is rarely if ever detected in air monitoring near the Great Lakes (Dann 1997).

If atmospheric loading of OCS can be assumed to be negligible, that leaves current external loading from point and non-point sources and internal loading from sediment inventories of past external loading. It is critical to differentiate between internal and external loading. External sources are generally controllable and likely to yield some benefits if controlled. Sediment inventories, on the other hand, are not readily easily controlled and will remediate naturally without further action.

The two different sources should produce different patterns over time and space. Systems whose OCS concentrations are tightly controlled by external sources should have very site specific and unique temporal patterns, because external source control will be a site-specific function of regulatory commitment, local economic conditions, amenability to control, and other site specific factors. Thus, if, as is often hypothesized, sites on the Niagara River are a major current source of OCS to the Lake Ontario, one would expect declines in OCS in the Niagara River and Lake Ontario media to be episodic, tied tightly to specific remediation activity. It is also expected that the temporal patterns of decline will be very different from OCS declines at other sites, and very different from declines of other chemicals with similar fate processes (e.g. PCBs and DDE) not associated with sources of OCS.

The patterns of decline for systems controlled by internal sediment stores are likely to be very different. As the fate processes controlling declines in sediments are relatively constant across time and space and across PTS chemicals, one would expect systems controlled by internal inventories to decline at fairly similar rates through time, and across

lakes and across PTS chemicals. The data, while limited, seem more consistent with the latter hypothesis. The very similar declines of OCS in the gull eggs across colonies suggests some common mechanism of decline (e.g, fate processes affecting sediment inventories.)

Great Lakes system dominated by internal sediment inventories should also have orderly declines of different persistent toxic substance. That is, concentrations of different organochlorines should decline in a predictable fashion based on the vulnerability to fate processes affecting concentrations in the sediments. More volatile and degradable chemicals like hexachlorobenzene should dissipate faster from the Great Lakes than more stable, less volatile chemicals such as Mirex and dieldrin. PCBs are of intermediate vulnerability and should dissipate with an intermediate speed. The predicted rates of relative decline for internal inventories of various organochlorine can be estimated from the model of Endicott et al. (1992a) under a condition in which external loading was reduced to zero. In this case, long-term declines of these chemicals depends on vulnerability to various loss processes. These estimated zero-loading declines can be compared to yearly declines observed for lake trout in Lake Ontario (Huestis et al. 1986). As can be seen from Figure 12, there is a significant relationship between predicted and observed declines of different organochlorines (regression analysis, $p < 0.05$). That is, as predicted, the different organochlorine are declining in a significantly orderly process, further supporting the hypothesis that external loading is unimportant. It is also important to note that OCS is actually declining faster than predicted. At the least, this graph demonstrates that OCS, which has received little regulatory attention in the last several decades is declining considerably faster than compounds like DDT, PCBs, and TCDD, which have been under very strict regulation. This observation is inconsistent with a system dominated by external sources, which ought to be more controllable.

There are other data to substantiate that current concentrations of OCS in Lake Ontario are based on internal sediment inventories as opposed to current external loading. Loading from the Niagara River can be estimated from the Upstream/Downstream monitoring. Best estimates of early 1990s loading from the Niagara River are about 4.3 to 6 grams per day, depending upon what values are assigned to non-detection data. According to Endicott et al, model, this loading of OCS should produce lake trout concentrations of about 5.2 to 3.8 ug/kg in whole lake trout. These predicted values are 6 to 8 times lower than observed concentrations for this period, about 31 ug/kg (Huestis et al. 1996). The discrepancy between observed and predicted concentrations also supports the hypothesis that OCS concentrations in Lake Ontario are largely due to internal sediment inventories, as opposed to current external loading.

Table 2. Summary of results. Decreases are based on regression analyses. ND means not detected.

Medium	Location	Time Frame	Decrease (% per year)	Most recent conc.
Gull egg	Lake Ontario	1987-1998	Yes (17%)	Some ND
Gull egg	Lake Erie	1987-1998	Yes (16%)	Some ND
Gull egg	Lake Huron	1987-1998	Yes (16%)	Some ND
Gull egg	Lake Superior	1987-1998	Yes (17%)	Some ND
Gull egg	Lake Michigan	1987-1998	Yes (20%)	Some ND
Gull egg	Niagara River	1987-1998	Yes (17%)	Some ND
Gull egg	Detroit River	1987-1998	Yes (20%)	Some ND
Spottail Shiner	Lower Niagara River	1985 -1995	Yes (8%)	100% ND
Spottail Shiner	Lake Ontario	1985 -1995	NA	100% ND
Lake Trout	Lake Ontario	1977-1993	Yes (10%)	0 % ND
Water	Niagara River	1989-1995	Yes (16%-21%)	50% ND
Water	Upper Niagara River	1989-1994	NA	100% ND
Water	Lake Ontario	1984, 1996	Yes (20%)	100% ND
Water	St. Clair River (Port Edward)	1989-1996	Yes (15%)	>95% ND
Water	St. Clair River (Port Lambton)	1989-1995	NA	10% ND
Water	St. Lawrence	1989-1996	NA	90% ND
Sediments	Lake Ontario	1960-1981 (95)	Yes (12%)	100% ND

CGLI appreciates the opportunity to provide these comments. We look forward to working with the Workgroup to correct the process and technical errors represented by the Battelle report.

Sincerely,

George H. Kuper, President
and CEO